Electronic Supplementary Material (ESI) for RSC Advances


# Schiff base supported MCM-41 catalyzed the Knoevenagel Condensation in water

Xiuzhi Dong, Yonghai Hui*, Shaolei Xie, Peng Zhang, Guangpeng Zhou, Zhengfeng Xie*

Key Laboratory of Oil & Gas Fine Chemicals, Ministry of Education, Xinjiang University, Urumqi 830046, People's Republic of China.

Fax : (+86)-991-8581-018 E-mail: xiezhf72@yahoo.com.cn; hyhai97@yahoo.com.cn

## Supporting Information

### Table of contents

**General Information.** All the commercial available reagents and the anhydrous solvents were purchased from Aladdin and used without further purification. The samples were analyzed using FT-IR spectroscopy (using a Bruker equinx 55 in KBr matrix in the range of 4000–400 $cm^{-1}$). The X-ray powder diffraction (XRD) of the catalysts was carried out on a instrument (Rigaku R-axis Spider, Japan) using nickel filtered Cu Kα radiation. Scanning electron microscope (SEM) studies were performed on LEO1430VP, Germany. Transmission electron microscope (TEM) images were obtained from a (Hitachi H-600, Japan) instrument. $^{1}$HNMR spectra were recorded on an INOVA 400 MHz FT-NMR spectrometer, using $CDCl_3$ as solvent and TMS as internal reference (chemical shifts, in ppm). $^{13}$CNMR spectra were collected at INOVA 400 MHz FT-NMR spectrometer, using $CDCl_3$ as solvent and TMS as internal reference (chemical shifts, in ppm). Mass spectroscopy data of the product was collected at a Hewlett-Packard HP1100 LC/MSD instrument. Purification of reaction products were carried out by column chromatography using Qingdao silica gel (300-400 mesh). Analytical thin-layer chromatography (TLC) was performed on silica gel GF254 (Qingdao, China) with ethyl acetate and petroleum ether (60-90 °C). Melting points were determined on an Elemental digital melting points apparatus and were uncorrected.

**Experimental Section**

General procedure for the synthesis of Schiff base supported MCM-41

The preparation of $\mathbf{L_1}$ and $\mathbf{L_2}$ were performed according to the previous literature[1] . $\mathbf{L_3}$ was prepared by the reaction of $\mathbf{L_2}$ (1 g) and 2-phenyl-2H-1,2,3-triazole-4-carbaldehyde (2 mmol) in ethanol (40 mL) in the presence of glacial acetic acid. Afterwards, this mixture was refluxed for 24 h, with continuous stirring, under dry nitrogen atmosphere. The solution was cooled to room temperature and the powder was filtered, washed with diethyl ether and dichloromethane.

General procedure for the synthesis of α,β-unsaturated dicyanides (**2a** as an example)

The reaction mixture of benzaldehyde (75 μL, 0.75 mmol), malononitrile (0.033 g, 0.5 mmol), $\mathbf{L_3}$ (0.005 g) was stirred at room temperature in water (1.5 mL) for 3 h. The mixture was extracted with dichloromethane (5×5 mL). Notably, the catalyst was still kept in the water phase and then the water phase was directly used for the next cycle.The combined organic phase was dried over anhydrous $Na_2SO_4$, filtered and concentrated by evaporation. The crude product was purified by Column chromatography on silica gel (petroleumether/ethyl acetate 30:1) to give product **2a** (76.3 mg, 99%) as a white solid.

**Physical data of compounds isolated**

**2a**: White solid: M.p. = 87-89 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.92 (m, 2H), 7.78 (s, 1H), 7.64 (m, 1H), 7.55 (m, 2H).

**2b**: White solid: M.p. = 133-134 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.81 (m, 2H), 7.72(s, 1H), 7.34 (m, 2H), 2.46 (s, 3H).

**2c**: Yiellow solid: M.p. = 88-89 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 8.19 (m, 1H), 7.58 (m, 1H), 7.08 (m, 1H), 6.09 (m, 1H), 3.92 (s, 3H).

**2d**: White solid: M.p. = 106-107 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.74 (s, 1H), 7.45 (m, 3H), 7.18 (m, 1H), 3.86 (s, 3H).

**2e**: Yiellow solid: M.p. = 117-119 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ = 7.91 (m, 2H), 7.65 (s, 1H), 7.01 (m, 2H), 3.91 (s, 3H).

**2f**: White solid: M.p. = 159-160 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ =7.85 (m, 2H), 7.73 (s, 1H), 7.52 (m ,2H).

**2g**: White solid: M.p. = 165-167 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ =7.77 (m, 2H), 7.70 (m, 3H).

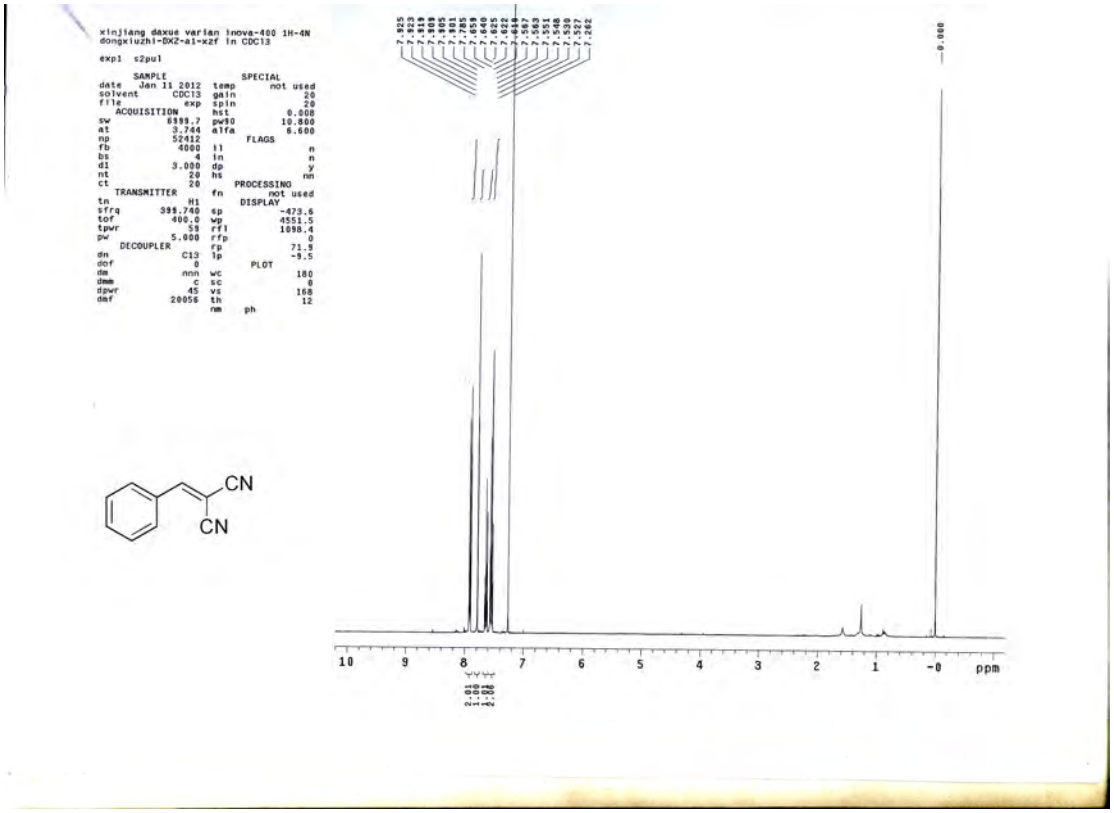
**2h**: White solid: M.p. = 129-130 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ =7.96 (m, 2H), 7.75 (s, 1H), 7.24 (m, 2H).

**2i**: Yiellow solid: M.p. = 73-75 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ =7.80 (m, 1H), 7.51 (s, 1H), 7.37 (m, 1H), 6.72 (m, 1H).

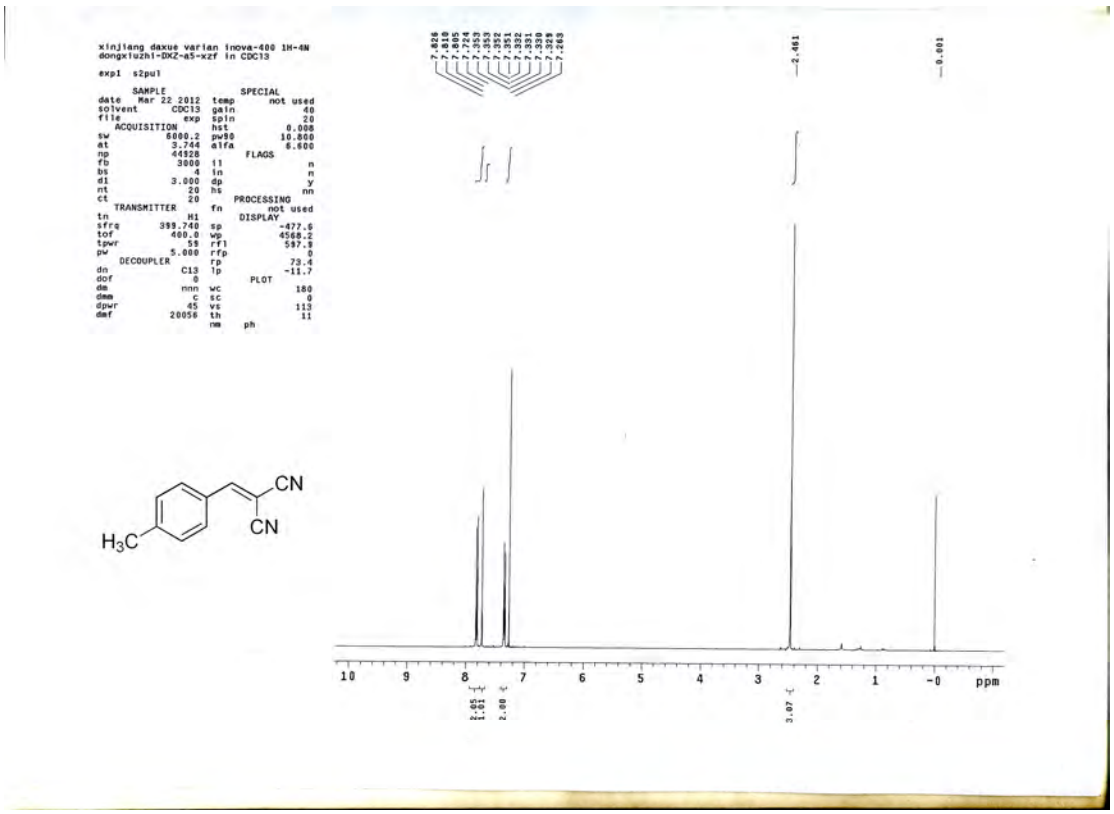
**2j**: Yiellow solid: M.p. = 160-161 °C; $^{1}$H NMR (400 MHz, $CDCl_3$): δ =8.52 (s, 1H),8.13 (m, 2H), 8.0 (s, 1H), 7.51 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 147.91, 141.25, 138.71, 137.54, 129.68, 129.55, 128.49, 119.57, 112.77, 112.14; MS: m/z = 222.1 [M+1], 246.2 [M+Na].

**2k**: Yiellow solid: M.p. = 172-173 °C; $^{1}$H NMR (400 MHz, $CDCl_3$): δ =8.65 (s, 1H), 8.27 (m, 1H), 8.11 (m, 1H), 7.96 (m, 2H), 7.51(m, 3H).

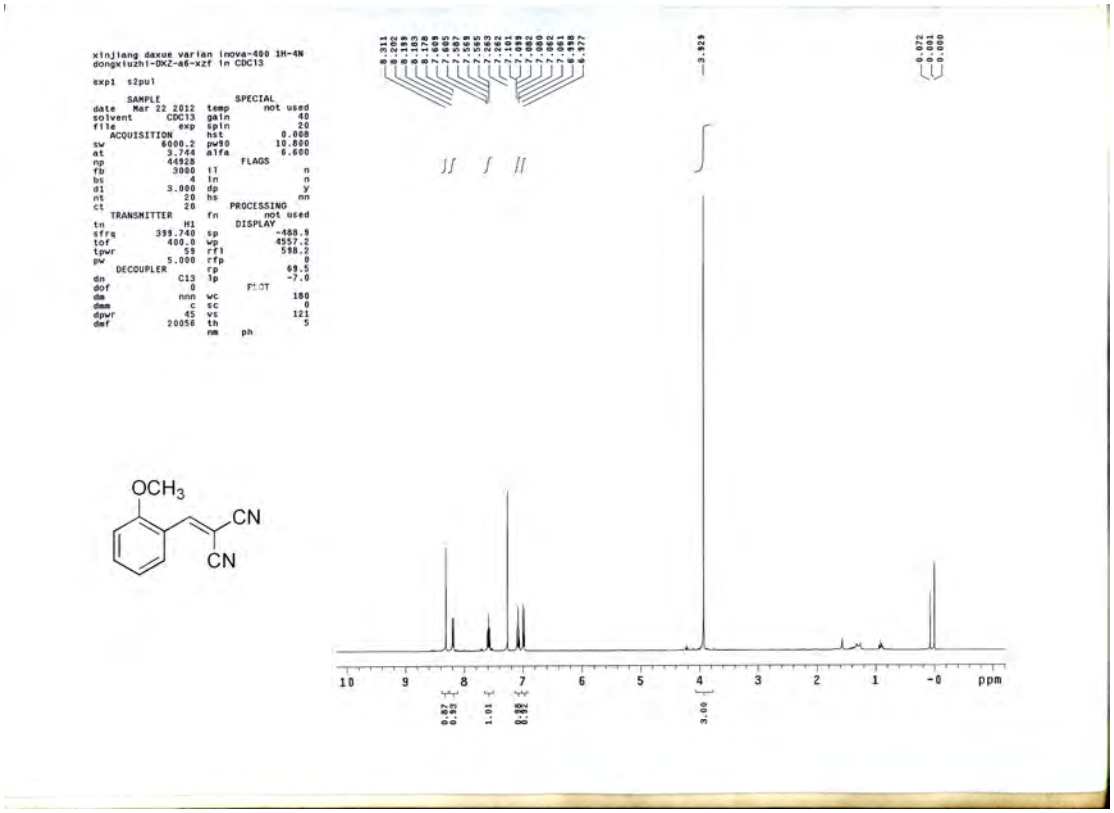
Compound **2a**



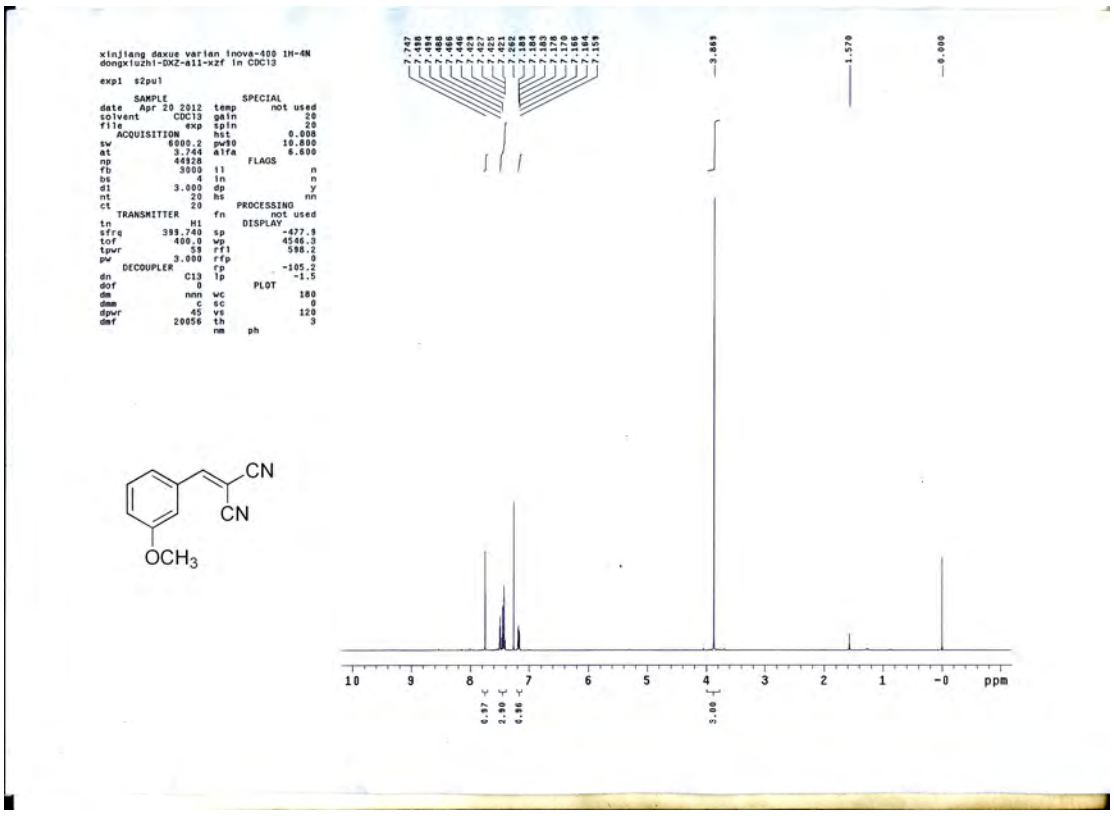

Compound **2b**



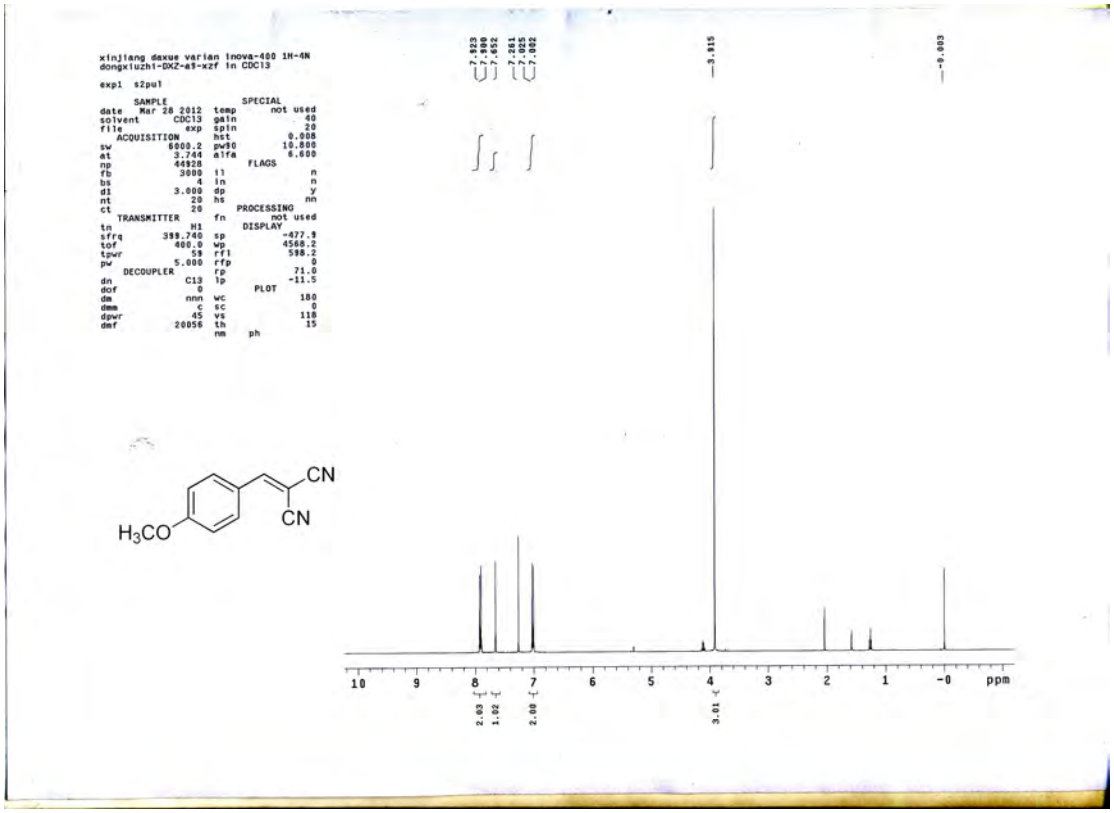
Compound **2c**



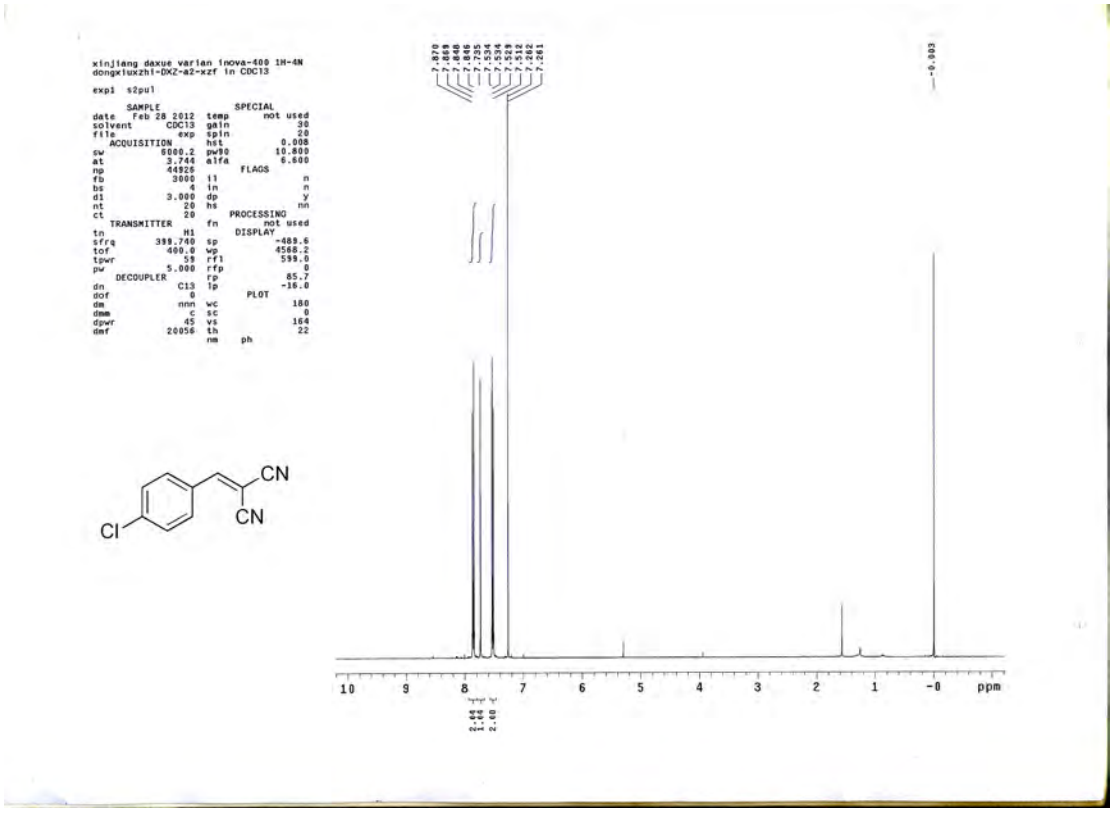

Compound **2d**



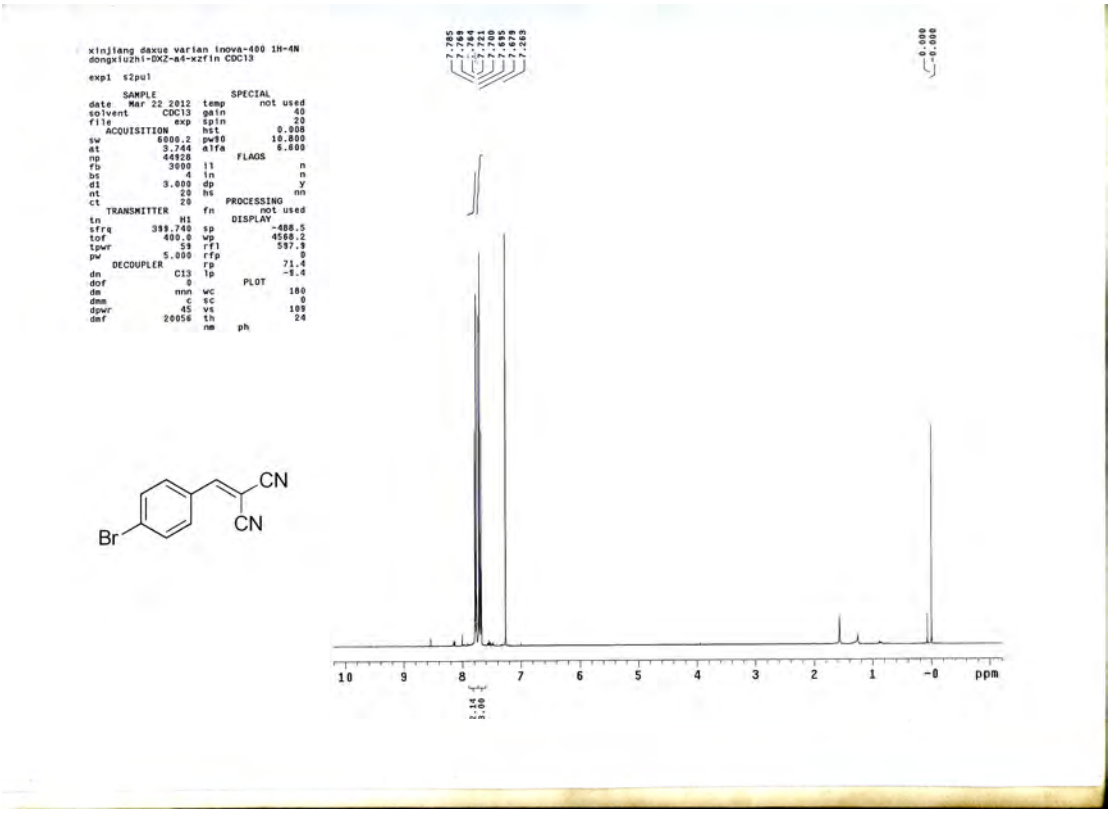
Compound **2e**



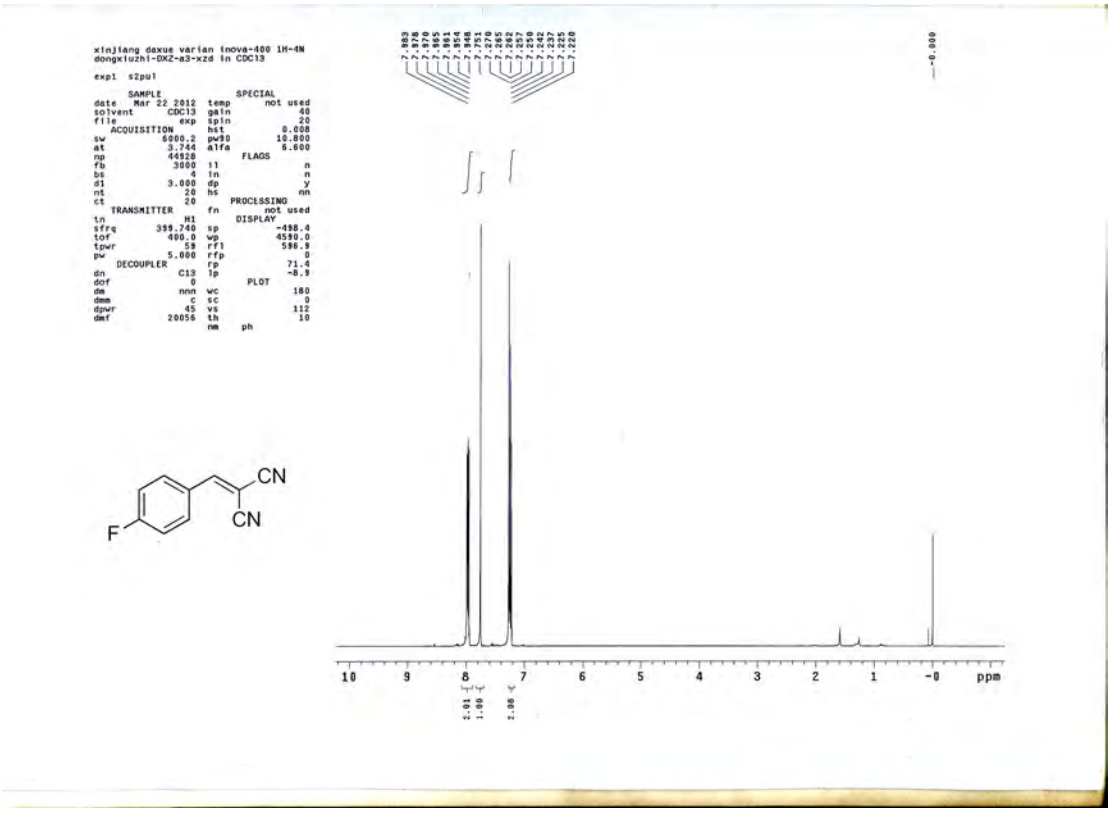

Compound **2f**



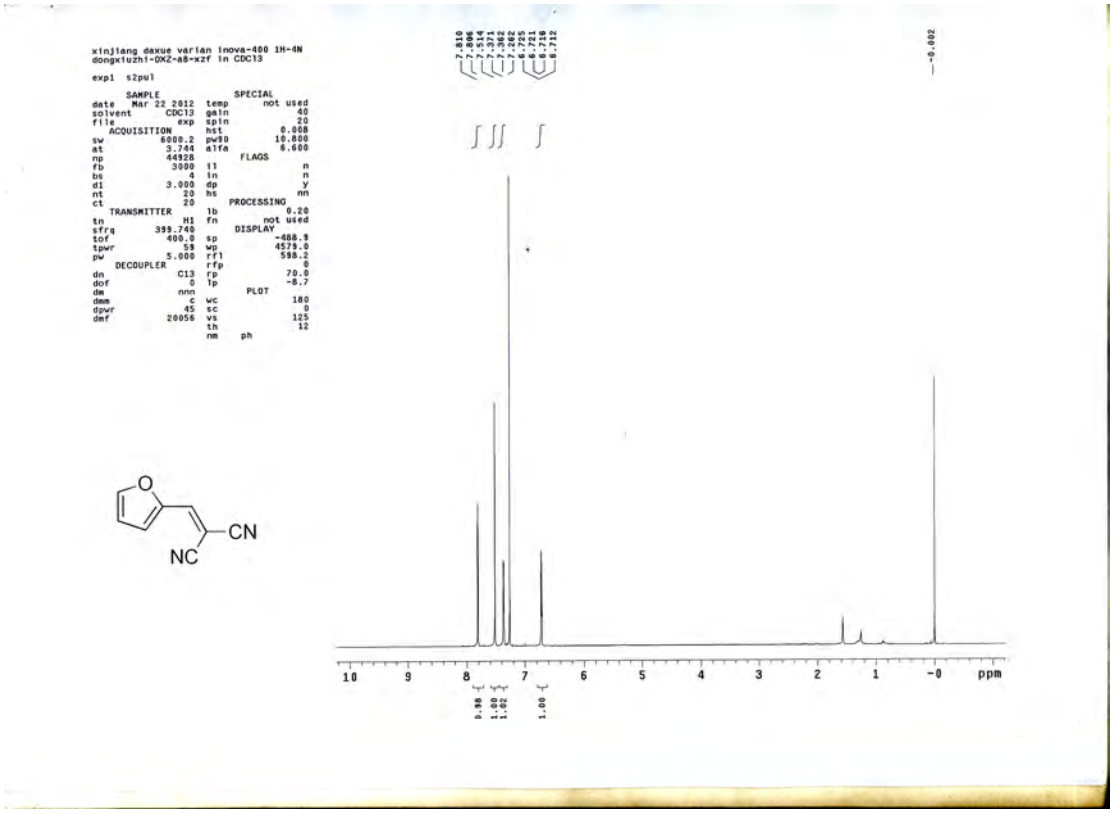
Compound **2g**



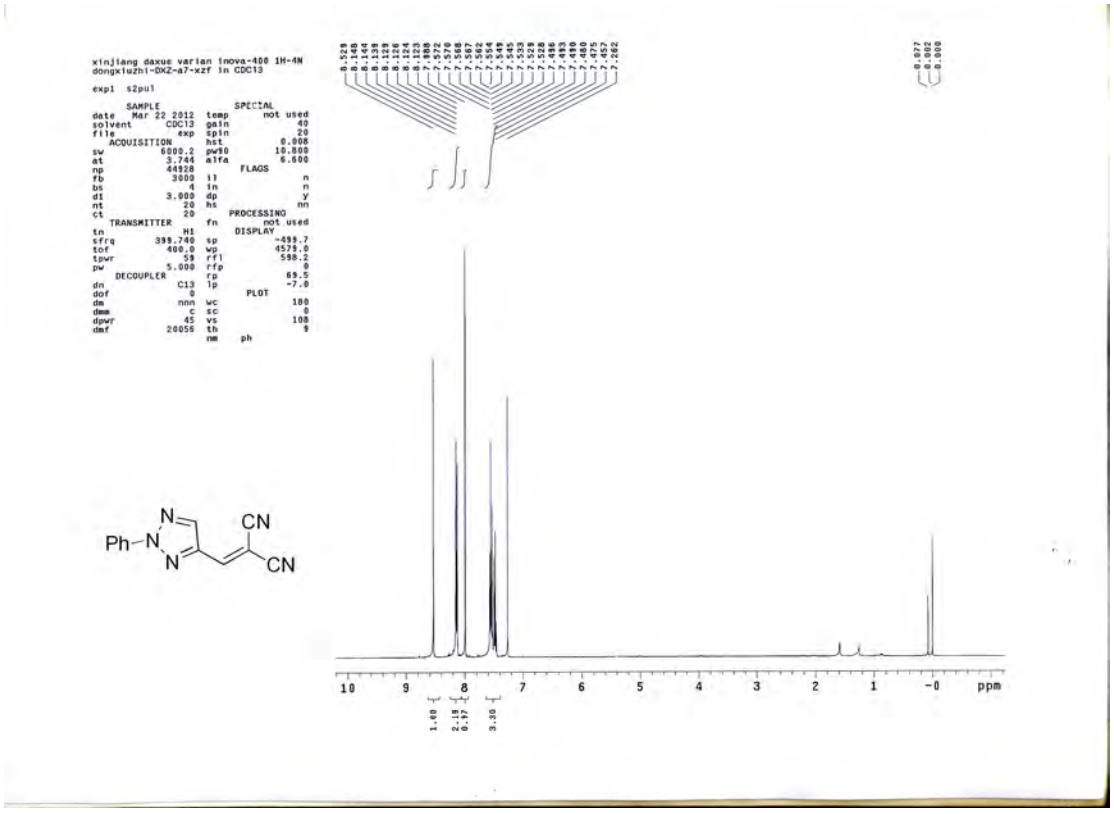

Compound **2h**

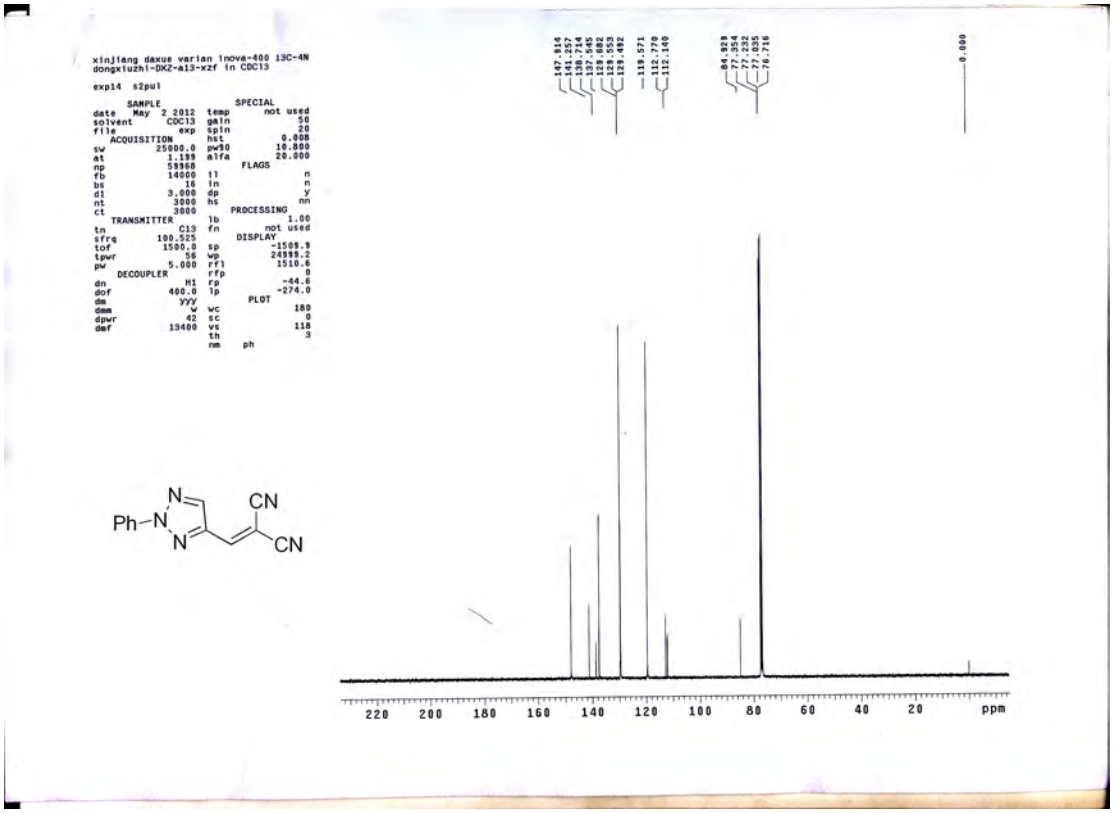


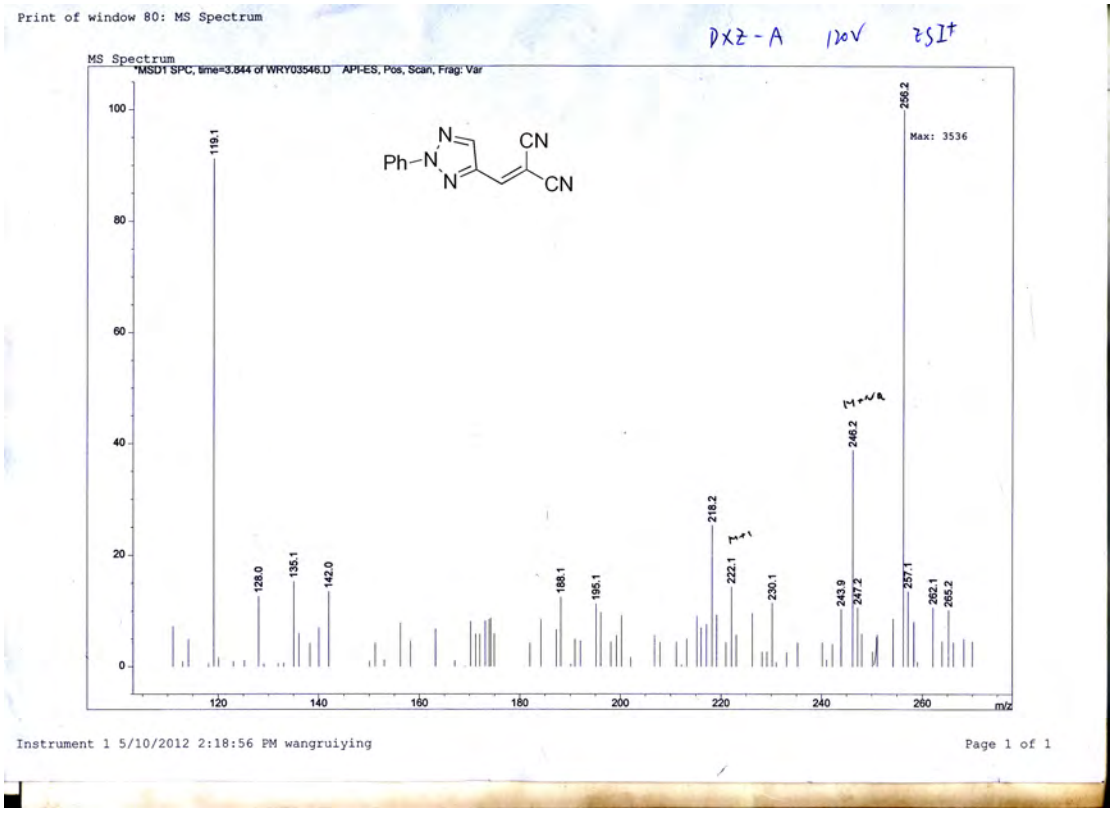
Compound **2i**



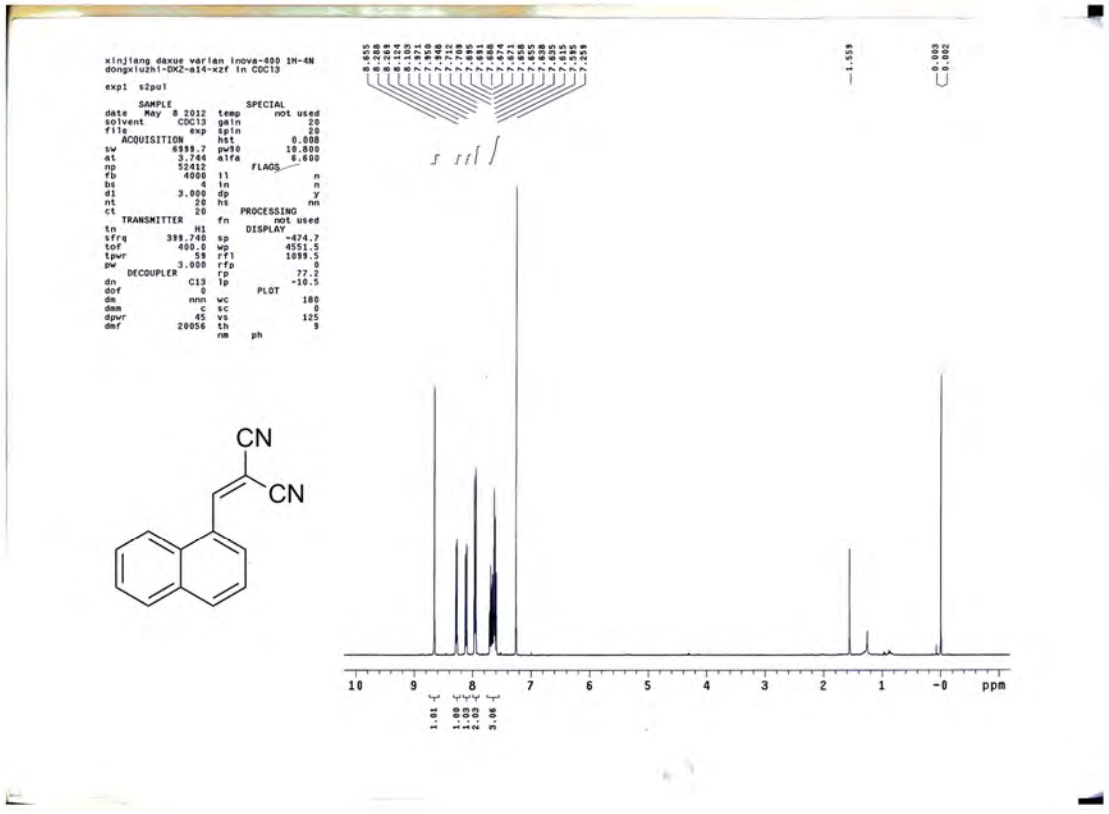

Compound **2j**




xinjiang daxue varian inova-400 13C-4N
dongxiuzhi-DXZ-a13-xzf in CDCl3
exp14 s2pul
SAMPLE
date May 2 2012
solvent CDCl3
file exp
ACQUISITION
sw 25000.0
at 1.199
np 59968
fb 14000
bs 16
d1 3.000
nt 3000
ct 3000
TRANSMITTER
tn C13
sfrq 100.525
tof 1500.0
tpwr 56
pw 5.000
DECOUPLER
dn H1
dof 400.0
dm yyy
dmm w
dpwr 42
dmf 13400
SPECIAL
temp not used
gain 50
spin 20
hst 0.008
pw90 10.000
alfa 20.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp -1509.9
wp 24999.2
rf1 1510.6
rfp 0
rp -44.6
lp -274.0
PLOT
wc 180
sc 0
vs 118
th 3
ph
147.814
141.257
130.714
130.345
129.682
129.553
129.492
119.571
112.770
112.140
84.928
77.354
77.032
76.710
0.000
Ph
N
N
N
CN
CN
220
200
180
160
140
120
100
80
60
40
20
ppm


Print of window 80: MS Spectrum
DXZ-A 120V 25t
MS Spectrum
"MSD1 SPC, time=3.844 of WRY03546.D API-ES, Pos, Scan, Frag: Var
Max: 3536
119.1
256.2
246.2
218.2
222.1
230.1
128.0
135.1
142.0
188.1
195.1
243.9
247.2
257.1
262.1
265.2
M+1
M+Na
Ph
N
N
N
CN
CN
100
80
60
40
20
0
120
140
160
180
200
220
240
260
m/z
Instrument 1 5/10/2012 2:18:56 PM wangruiying
Page 1 of 1

Compound **2k**




**Reference**

1 P. Oliveira , A. Machado, A. M. Ramos, I. Fonseca, F. M. Braz Fernandes, A. M. Botelho do Rego and J. Vital, Microporous and Mesoporous Mater., 2009, 120, 432.